

Original Paper

STUDY OF METAL CONTAMINANT LEVEL IN THE MAHAKAM DELTA: SEDIMENT AND DISSOLVED METAL PERSPECTIVES

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ABSTRACT

The Mahakam Delta in East Kalimantan contains large number of natural resources specially hydrocarbon sources. Anthropogenic activities have influenced this ecosystem for many years. The aims of this work were to find out dissolved metal and metals in sediment distribution in this area and to find out contaminant level based on allowable guidelines. Twenty nine stations were sampled within the delta and metal content analyses, both in sediment and water column, were established for Cd, Cu, Ni, Pb and Zn. Sediment analyses were conducted using US EPA 3050B method and dissolved metals analyses were conducted using Back Extraction method. Cd, Cu, Ni, Pb and Zn in sediment had 0.07 mg/kg dw, 18.64 mg/kg dw, 35.62 mg/kg dw, 10.56 mg/kg dw and 74.95 mg/kg dw in maximum concentration respectively. Whereas dissolved Cd, Cu, Ni, Pb and Zn had 0.001 mg/l; 0.003 mg/l; 0.003 mg/l; 0.013 mg/l and 0.003 mg/l in maximum concentration respectively. Based on allowable guidelines, metals contaminant levels, both in sediment and water column, were below permitted value.

Keywords: Mahakam delta, Metals, sediment and water column

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INTRODUCTION

Estuarine systems are among the most productive and dynamic ecosystems on earth. Coastal and estuarine watersheds currently support 75% of the world's population and are still rapidly being developed (Corbett et al., 2009). Water and sediment quality which is vital for the survival and well being of the living resources, especially in the coastal and estuarine areas, is governed by many factor including heavy metals. Knowledge of distribution and concentrations of heavy metals in the sediments will help detect the source of pollution in the aquatic systems (Nobi et al., 2010). The concentration of metals found in sediments is the result of natural phenomena, anthropogenic activities or the combination of both (Munoz-Barbosa et al., 2012; Varol, 2011). In addition, sediments play a major role in the overall fluxes of trace elements in coastal systems, acting occasionally as a source and/or sink (Guo et al., 2010; Sakellari et al., 2011). Many researcher believed that the sediments

were indicator for water pollution and the distribution of heavy metals in the sediments could reflect the water pollution level (Guo et al., 2010).

Sea water contains low concentration of most metals in solution and can be modified regionally through volcanic activity, meteorization and/or erosion of the detritus phases of the rocky basement and fluvial contribution. Although rivers transport small amounts of dissolved metals, these can alter the natural proportion of local sea water by dilution or enrichment of some major and minor cations (Ahumada et al., 2011).

Metal contamination in aquatic environments has received huge concern due to its toxicity, abundance and persistence in the environment and subsequent accumulation in aquatic habitats (Luoma and Rainbow, 2008; Guo et al., 2010; Varol, 2011). Heavy metal residues in contaminated habitats may accumulate in microorganisms, aquatic flora

mangrove forests declined drastically (Husain, 2006).

The purpose of the study were determining Cd, Cu, Ni, Pb and Zn distribution in water column and bottom sediment contents of Mahakam delta and its contaminant level due to allowable guideline.

Sampling Site

Sediment samples were collected at 29 stations in Mahakam Delta along geographical area of $117^{\circ}15'-117^{\circ}35'$ E dan $0^{\circ}20'-0^{\circ}57'$ S (**Fig. 1**) located using the Global positioning System (Garmin GPS). In each station, sediment sample was taken with a *Ponar Grab* and homogenous mixing of surface sediment (0-10 cm) was formed. Sediment samples were transported to the laboratory under cooling condition (Hutagalung et al., 1997; Lestari and Witasari, 2010). Water samples were taken with water sampler *van dorn* at 0.5 m in depth and were filtered using $0.45\ \mu\text{m}$ Whatmann filter paper then preserved using 1 mL HNO_3 / 1L sample.



Analitical Procedure

All Analyses were conducted in heavy metal laboratory, Research Center for Oceanography LIPI according to USEPA 3050B methods. Collected sediment was heated at 105°C then a gram of dry sediment was weighed and destructed using three kind of acids. The addition of nitric acid (1+1), concentrated nitric acid, H₂O₂ and concentrated hydrochloric acid were simultaneously established to destruct sediment sample. Sample solution was heated in hotplate in vary heating time. Destructed sample was filtered with whatman No. 41 and was diluted to 100 mL aquadest. On the other hand, water samples were analyses using *Back Extraction* Method (Standard Method, 1992). 250 mL sea water (pH 3-3,5) were extracted using 2.5 mL of 4% Ammonium pyrrolidine dithiocarbamate and 25 mL sodium diethyl dithiocarbamate/ methyl isobuthyl ketone. Collected extract was rinse by aquadest and destructed using 0.25 mL concentrated HNO₃. Both sediment and sea water sample solutions were analyzed using Atomic Absorption Spectrophotometer Varian SpectAA 20.

Data Analysis

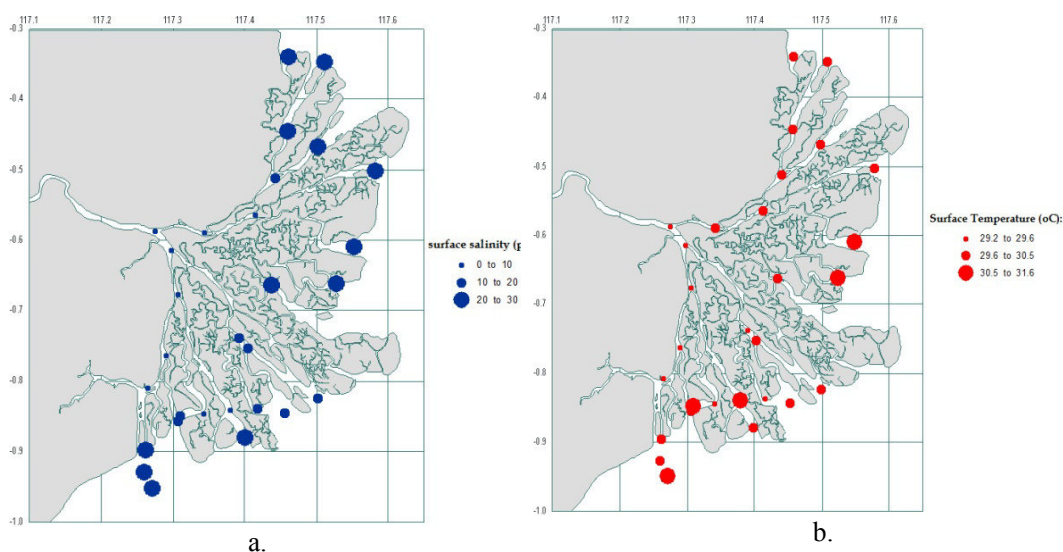
Pearson's correlation was used to understand the association of metals with physical

parameters. On the other hand, the contaminant level of Cd, Cu, Pb, Ni and Zn were assessed by comparing with quality guideline, Indonesian and Australian water quality guideline for dissolved metals and Canadian sediment quality guideline for metals in sediment.

RESULTS AND DISCUSSION

Results

Salinity and temperature showed tropical estuarine characteristics (**Figure 2**). Salinity and temperature measurement was taken in surface and bottom water column. Minimal salinity in the surface water was 0.03 psu at upper river and increasing towards the estuary, 29.21 psu as the maximum value, 15.71 psu in average. There were no significant surface water temperature differences between stations, in the range of 29.30°C-31.5°C (**Figure 2a and b**). Bottom waters had higher temperature and higher salinity than surface waters. Water column had 29.86 °C in average bottom temperature and 19.22 psu in average bottom salinity.



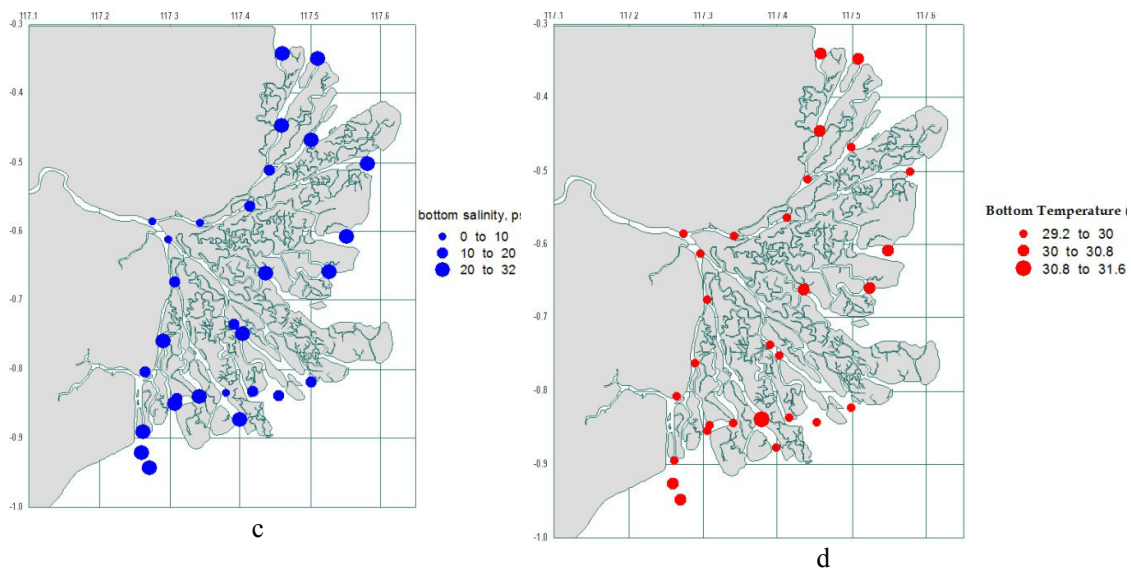
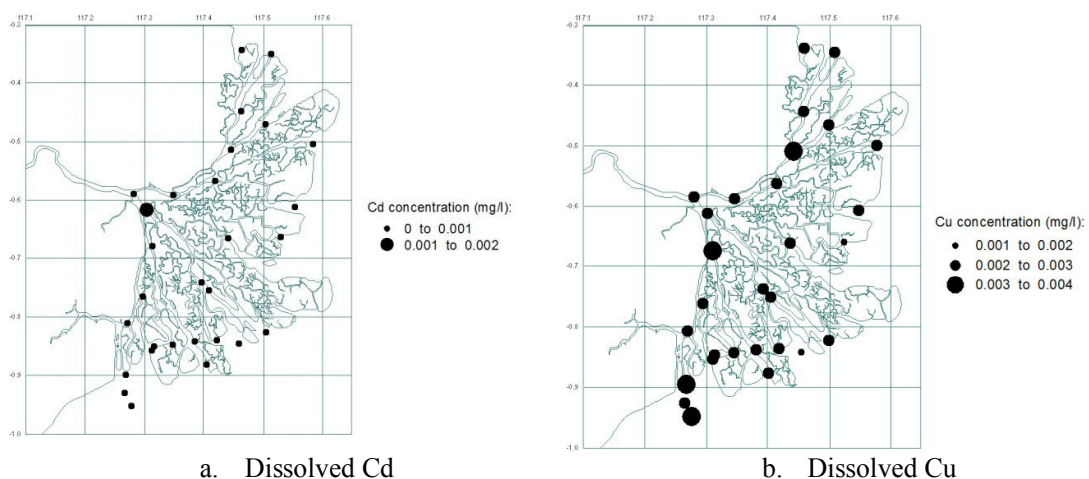


Fig. 2. Distribution of surface water salinity (a), surface water temperature (b), bottom salinity (c) and bottom temperature (d)

Heavy metal in water analyses were conducted for Cd, Cu, Pb, Ni and Zn. The obtained data represented Cd less than 0.001 mg/L in entire stations except for station 2, 0.001 mg/L (**Fig. 3a**). Cd spread evenly in the delta areas however Cu and Ni seem to be distributed in the south of the Delta. River stream to Muara Jawa showed relatively high concentration of

both Cu and Ni, 0.003 mg/L in maximum concentration and 0.002 mg/L in average concentration (**Fig. 3b and 3c**). Pb detected 0.013 mg/L in maximum concentration and 0.009 mg/L in average concentration (Fig 3d). Whereas, maximum Zn concentration, 0.003 mg/L, identified in the North stream (**Fig 3.e**)



a. Dissolved Cd

b. Dissolved Cu

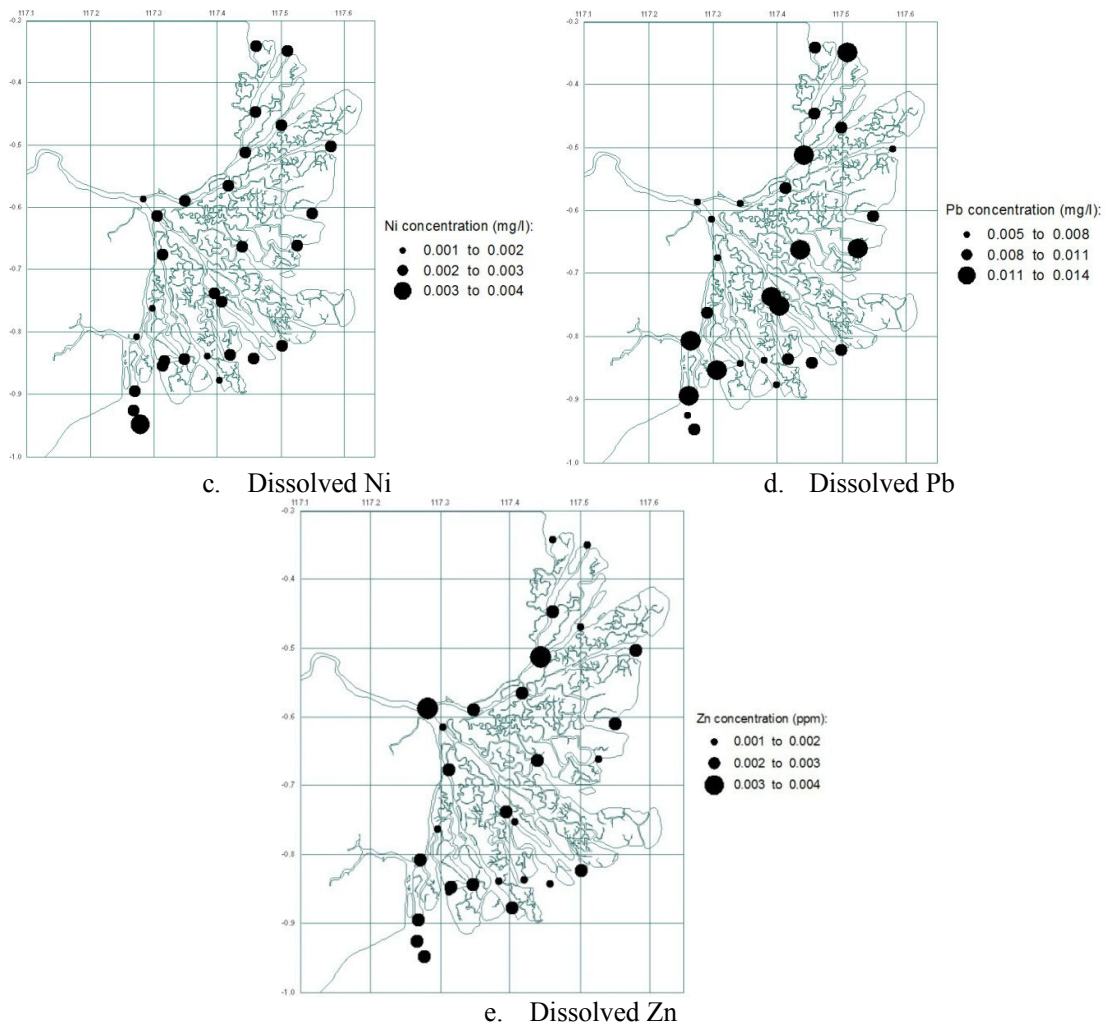
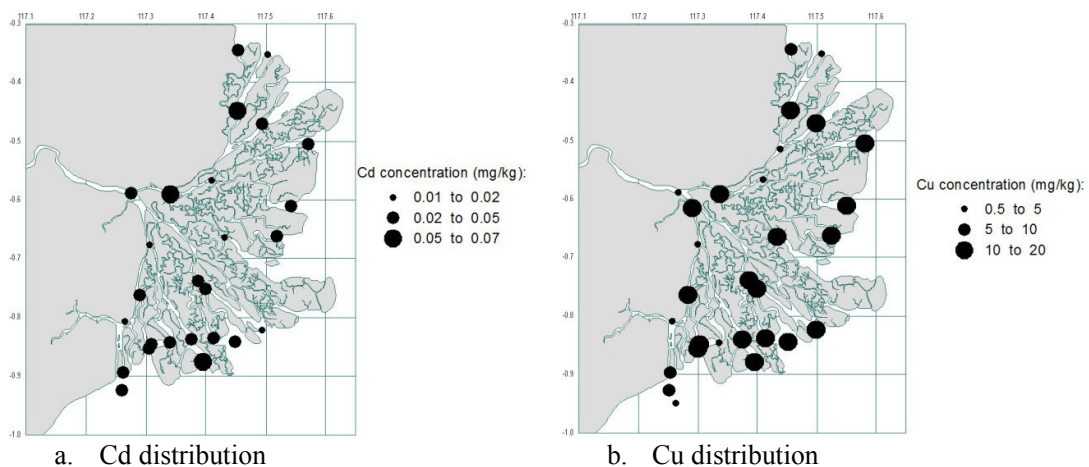


Fig 3. Dissolved metals distribution in the Mahakam delta

Cd, Cu, Ni, Pb and Zn were analyzed in sediment of The Mahakam Delta. Those metals distributed at the river mouth in preference. Cd, Cu, Ni, Pb and Zn have 0.07 mg/kg dw, 18.64

mg/kg dw, 35.62 mg/kg dw, 10.56 mg/kg dw and 74.95 mg/kg dw in maximum concentration respectively (**Fig 4**).



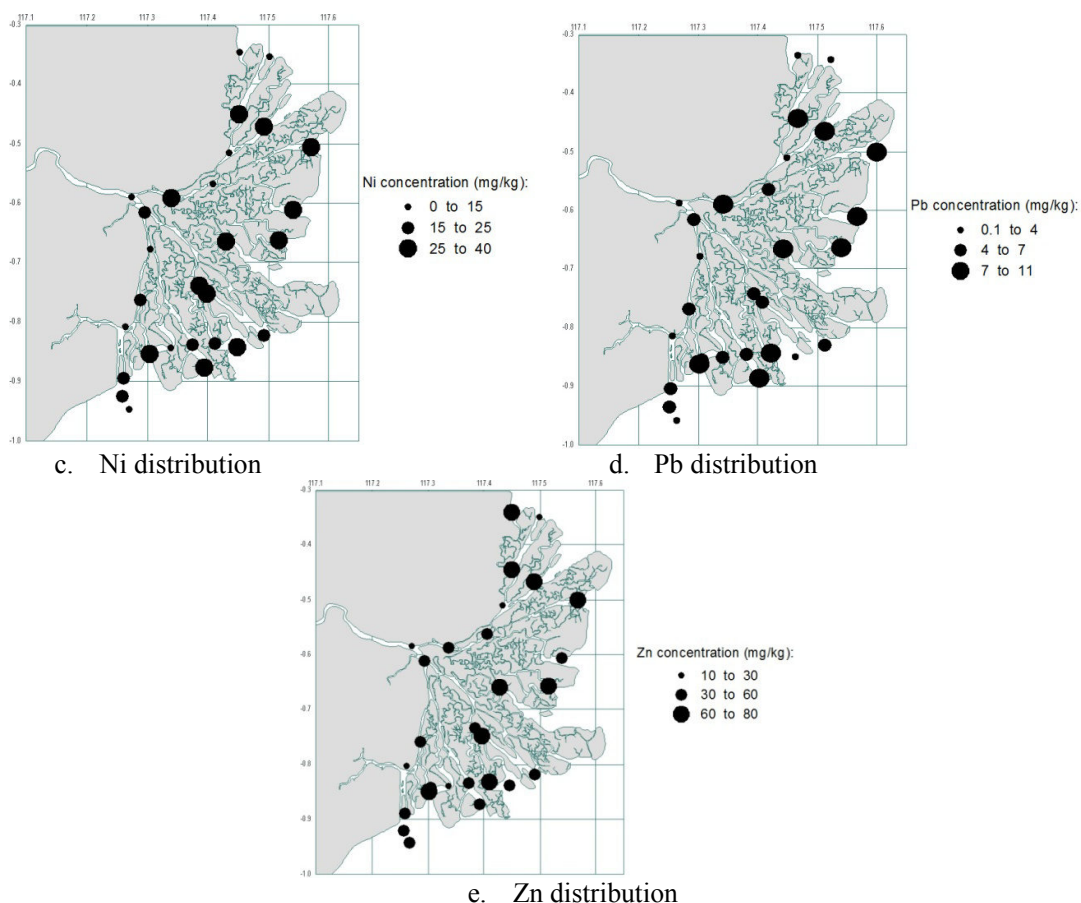


Fig 4. Heavy Metals distribution in sediment

Pearson correlation was conducted to identify salinity effect on dissolved metals pattern and the result, no significant correlation was detected (**Table 1**). Dissolved Cd, Cu and Zn

indicated negative correlation with dissolved Pb, Ni, Temperature and salinity.

Table 1. Pearson Correlation for temperature, salinity and dissolved metals.

	temperature	salinity	Pb	Cd	Cu	Zn	Ni
temperature		0.374	0.081	-0.246	-0.097	-0.190	0.156
salinity			0.331	-0.329	-0.116	-0.153	0.367
Pb				-0.268	0.145	-0.055	0.150
Cd					-0.029	-0.220	0.060
Cu						0.468	0.226
Zn							-0.032

Comparing with another estuary, Mahakam delta was quite similar with Port Jackson, Australia (**Table 2**). However, this

concentrations were still below the guideline limit (**Table 3**).

Table 2. Dissolved Metals concentration ($\mu\text{g/l}$) from Mahakam delta and other coastal zones

Element	Location		
	Mahakam Delta	Open Coastal Pacific Ocean	Port Jackson, Australia
Cd	<1 - 1	0.01	0.006 - 0.104
Cu	1 - 3	0.09	0.932-2.55
Ni	1 - 3	0.2	0.175-1.61
Zn	1 - 3	0.2	3.27-9.66
Reference	This Study	(Batley, 1996 in Hatje et al., 2003)	Hatje et al., 2003

Table 3. General acceptable levels of dissolved metals for marine environment ($\mu\text{g/l}$)

Country	Treshhold ($\mu\text{g/l}$)					Refference
	Cd	Cu	Ni	Pb	Zn	
Indonesia:	1	8	50	8	50	Indonesian Ecological Ministry, 2004
Australia and New Zealand	<0.5 – 5		< 100	<1-7.0		ANZECC, 2000
ASEAN	10			8.5		AMEQC, 1999

Metals in sediment showed non conservatives behaviour and showed no significant correlation with temperature (**Table 4**). However, metals in sediment indicated varying

correlation each others. Pb showed strong correlation with Cu, Zn and Ni.

Table 4. Pearson Correlation for Temperature, Salinity and Metals in sediment.

	Temperature	Salinity	Pb	Cd	Cu	Zn	Ni
Temperature		0.096	0.010	-0.156	0.110	0.245	0.223
Salinity			0.268	0.229	0.267	0.458	0.276
Pb				0.329	0.851	0.682	0.779
Cd					0.503	0.393	0.469
Cu						0.861	0.951
Zn							0.900

Maximum metals concentrations were below permitted guideline. However, maximum Cu

concentration almost reached ISQG allowable value (**Table 5**).

Table 5. Comparison of guideline metal in sediment and maximum concentration in this study (mg/kg dry weigh)

Treshold		element				
		Cd	Cu	Ni	Pb	Zn
Max conc in this study		0.07	18.64	35.62	10.56	74.95
CCME, 1999	ISQG	0.7	18.7		30.2	124.0
	PEL	4.2	108.0		112.0	271.0

Discussion

Trace metals availability, spatial distribution and behaviour are highly regulated by hydrodynamics, biogeochemical processes and

environmental conditions (redox, pH, salinity and temperature) of individual system (Eggleton and Thomas, 2004). Furthermore, trace metal partitioning between dissolved and particulate phases depend on not only

environmental condition but dissolved organic carbon and composition of the suspended particulate matter also (Hatje et al., 2003). Chemical characteristic can vary over time and by location and can be impacted by increasing anthropogenic input (DePalma et al., 2011). In estuaries, the mixing of freshwater high in trace metal concentrations with low concentration marine water may have a dilution effect on metal concentrations (Apeti et al., 2009).

Mahakam delta showed non conservative behaviour of dissolved metals. Dissolved Cd represented the equitable distribution. dissolved Cu, Ni and Pb tend to accumulate in the mouth of river. Dissolved Zn distributed in the north. There were no significant correlation showed between dissolved metals. This result supported Beck et al., (2010) report which indicated geochemical cycles occurring at the interface between terrestrial and marine groundwaters, called subterranean estuary, are not well understood for most elements. The widespread of anthropogenic sources of metals in the estuary may explain non conservative behaviour of dissolved metals. Hence, there is no universal pattern of trace metal behaviour in estuaries (Hatje et al., 2003).

Dissolved metals distribution in Mahakam delta in this study were higher than open coastal ocean. Average dissolved metal concentrations were roughly up to 10 times higher than open ocean. This means, terrestrial input played an important role of dissolved metal distribution. Station 2 indicated high concentration of dissolved Cd due to anthropogenic release of Cd by high fuel combustion in that area. It is well understood that Cd is soluble in water longer than other metals, this is due to complex formation with chlorine and other anions may inhibit the adsorption of cadmium in Fe oxide/hydroxide (Eggleton and Thomas, 2004).

Dissolved Pb concentration reached the highest level of all dissolved metals. The useful physical properties of Pb have resulted in multiplicity of uses of the metal (Ratcliffe, 1981). Mahakam delta's anthropogenic activities lead to high release of this metal. Oil and gas transport activities contributed Cd distribution in water column considering Darmono (1995) explanation that Cd found in crude oil.

Dissolved cadmium reported having correlation with dissolved zinc (Hendry et al., 2008; Lane et al., 2005; Ellwood, 2004). Zinc is used in zinc carbonic anhydrase to achieve optimal growth rate. In Zn limited condition, Cd substitutes Zn in carbonic anhydrase to maintain growth rate. Dissolved Cd has similar spatial distribution pattern to PO_4^{3-} in open ocean deep and surface water and this labile nutrient associated with organic matter (Morel and Price, 2003). Morel and Price (2003) concluded that the high Cd/ PO_4^{3-} of the coastal water is a consequence of two factors: the high input from terrestrial and continental shelf sediments and changes in biological fractionation with respect to P during uptake in region of high Fe and Zn.

Dissolved Cu and Ni correlated to aquaculture activities. Its enrichment was contributed by anti-foulant product and feeding. Manufactured feeds can contain zinc, copper, cadmium, iron, manganese, cobalt, nickel, lead, magnesium, selenium and mercury (Lorentzen and Maage, 1999).

Metals in sediment showed non conservative behaviour and showed no significant correlation to temperature. This probably caused by anthropogenic activities release metals to waters. The spatial pattern of metal distribution in sediment could be described in terms of distance from pollutant point source (Ward et al., 1986). However, in riverine system metals would be adsorbed into particulate matter (organic and inorganic) then precipitated and probably distributed through river stream. Sediment high concentration metal accumulated in the river mouth as an effect of fluvial transport.

Pb showed significant correlation to Cu, Zn and Ni whereas only Cd showed no significant correlation. In river water, Cd is usually adsorbed onto suspended particles. However, during estuarine mixing at the head of estuary, Cd in particulate phase is released into the water as dissolved phase, while in more saline environments complex-formation with chloride is chemically favored (Apeti et al., 2009). Cd readsorption is inhibited by chlorine.

Metals concentrations in all stations indicated below permitted guideline. Based on PEL value all metal concentrations had no effect on organisms. However, maximum Cu concentration almost reached ISQG allowable value. Cu is widely used as anti-foulant

additive (Lorentzen and Maage, 1999) and sailship activities influenced Cu input. Mahakam delta had dense of river transportation influenced Cu abundance in aquatic environment.

In aquaculture areas, particulate organic material (uneaten feed, faeces and bio-fouling biomass detached from cage structures) settle on seabed where it was degraded by microbes utilizing a variety of electron acceptors (Dean et al., 2007). Reported Elevated level of zinc and copper have been found in fish farm sediments. This report suggested that the zinc and copper sediment enrichment around fish farms was a result of feed and faeces inputs, and anti-foulant products (Brook and Mahnken, 2003).

Zhuang et al., (1994) explained that changes in sediment chemistry affect in contaminant remobilisation. Natural event, such as tidal movement and storm, and anthropogenic activities influenced, such as dredging, dredge disposal and fishing influenced remobilisation of sediment-associated contaminant (Eggleton and Thomas, 2004; Nascimento et al., 2006).

CONCLUSIONS

Mahakam delta have influenced by anthropogenic activities and metals content in this delta, both dissolved state and precipitated stated, was affected by metal input from terrestrial area. Furthermore, many guidelines from other countries used to assess metals contaminant level in the Mahakam Delta. As the result, Conducted comparison indicated that both metal in sediment and dissolved metal were below guidance limit. To achieve aquatic environment health, anthropogenic activities in Mahakam delta should be controlled.

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